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<p>(21) International Application Number: PCT/GB96/00218</p> <p>(22) International Filing Date: 5 February 1996 (05.02.96)</p> <p>(30) Priority Data: 9502587.0 10 February 1995 (10.02.95) GB</p> <p>(71) Applicant (for all designated States except CA FR US): SOF-ITECH N.V. [BE/BE]; Rue de Stalle 140, B-1180 Brussels (BE).</p> <p>(71) Applicant (for CA only): SCHLUMBERGER CANADA LIMITED [CA/CA]; Monenco Place, 24th floor, 801 6th Avenue, S.W., Calgary, Alberta T2P 3W2 (CA).</p> <p>(71) Applicant (for FR only): COMPAGNIE DES SERVICES DOWELL SCHLUMBERGER S.A. [FR/FR]; 50, avenue Jean-Jaurès, F-92541 Montrouge (FR).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): REID, Paul, Ian [GB/GB]; 35 Gainsborough Avenue, Eaton Ford, St. Neots PE19 3RJ (GB). CRASTER, Bernadette [IE/GB]; 31 Enniskillen Road, Cambridge CB4 1SQ (GB).</p>		<p>(74) Agent: MIRZA, Akram, Karim; Schlumberger Cambridge Research Ltd., High Cross, Madingley Road, Cambridge CB3 0EL (GB).</p> <p>(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> With international search report.</p>
(54) Title: DRILLING FLUID		

(57) Abstract

A water-based drilling fluid (WBM) comprises as additive one or more polyalkylene glycols or alcohol alkoxylates including butylene oxide monomer. Three typical additive molecules suitable for use in the drilling fluid of the invention are:  $\text{HO}(\text{EO})_7(\text{PO})_2(\text{BO})_2\text{H}$ ,  $\text{RO}(\text{EO})_5(\text{BO})_2\text{H}$ , where  $\text{R} = \text{C}_4\text{H}_9$ . Drilling fluids in accordance with the invention have been found in laboratory tests to exhibit improved shale inhibition properties as compared with known polyol containing WBM, particularly in the absence of added potassium ions. This is environmentally advantageous.

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## Drilling Fluid

This invention concerns drilling fluids, particularly water-based drilling fluids.

### Background to the Invention

Drilling fluids are used in well drilling operations, eg during drilling of oil and gas wells. During drilling, drilling fluid is pumped down a drillstring, discharged through ports in the drill bit and returned to the surface via the annulus between the drillpipe and the surrounding formation. The drilling fluid performs a variety of functions including cooling and lubricating the drill bit and drillstring, removing rock cuttings generated during the drilling process and carrying them to the surface, suspending cuttings in the annulus when pumping stops, preventing squeezing in or caving of the formation and keeping formation fluids at bay.

Drilling fluids generally comprise a carrier, a weighting agent and chemical additives. Drilling fluids fall into two main categories: water-based drilling fluids, also known as water based muds (WBM), in which the carrier is an aqueous medium; and oil-based drilling fluids, also known as oil-based muds (OBM), in which the carrier is oil. OBM are technically superior to WBM in certain important respects, including the comparative lack of adverse reactivity of OBM with shales, one of the most commonly encountered rock types during drilling for oil and gas. Use of OBM, however, has the disadvantage of resulting in production of large quantities of oil-contaminated waste products such as cuttings that are difficult to dispose of in an environmentally acceptable way. While use of WBM is environmentally more acceptable than OBM, the performance of WBM, particularly when drilling through water sensitive rocks such as shales, is technically inferior to that of OBM. Shales exhibit great affinity for water, and adsorption of water by shales causes the shale to swell and produces chemical changes in the rock which produce stresses that weaken the formation, possibly leading to erosion of the borehole or loss of structure. This can lead to drilling problems such as stuck pipe. In addition inferior wellbore quality may hinder logging and completion operations.

Much effort has been put into improving the performance of WBM relative to shales, namely improving the level of so called shale inhibition of WBM. Various chemical additives have been incorporated in WBM in attempts to improve shale inhibition. In particular water soluble glycols or polyols (ie. molecules containing more than one hydroxyl groups) are widely used for this purpose, typically being added to WBM in amounts in the range 3 to 10% by weight. Polyols used in this way include, for example, glycerols, polyglycerols, glycols, polyalkylene glycols (PAG), eg polyethylene glycols

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(PEG), polypropylene glycols (PPG) and copolymers of ethylene and propylene glycols, alcohol ethoxylates (AET) and glycol ethers. A typical inhibitive AET is an n-butanol derivative of ethylene oxide. The PAGs can have a range of ethylene oxide: propylene oxide (EO:PO) ratios and can be random or block copolymers; a frequently used material of this type is understood to be a random copolymer with an EO:PO ratio of about 1:1. See, for example EP 0495579, US 4830765, US 4172800. For further discussion of this subject see, for instance, The Society of Petroleum Engineers Reports SPE 25989 (Reduced Environment Impact and Improved Drilling Performance With Water-Based Muds Containing Glycols) and SPE 28818 (Water Based Glycol Drilling Muds - Shale Inhibition Mechanisms) and also Schlumberger Oilfield Review, April 1994, pages 33 to 43 (Designing and Managing Drilling Fluid).

The shale inhibition properties of polyol-containing WBM can be enhanced by incorporation of potassium salts, eg potassium chloride, possibly in combination with gypsum. However, the shale inhibition properties of even the best known potassium and polyol-containing WBM are much inferior to those of OBM. Further, the use of potassium can present waste disposal problems, as there are certain regions, eg. The Gulf of Mexico, where the discharge of potassium to the environment is prohibited or severely restricted. In addition, the use of potassium-containing WBM can present problems in land drilling where the contamination of ground water by potassium-containing drilling waste is considered unacceptable.

It has now been found that the shale inhibition properties of WBM can be improved by use of novel polyol additives in the form of various glycols and alkoxyates comprising butylene oxide monomer.

#### Summary of the Invention

According to the present invention there is provided a water-based drilling fluid comprising as additive one or more polyalkylene glycols or alcohol alkoxyates including butylene oxide monomer.

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Polyalkylene glycols (PAGs) are addition polymers of alkylene oxides. While it is known to use PAGs based on ethylene oxide (EO) and propylene oxide (PO) monomers, eg in the form of EO homopolymers (polyethylene glycols), PO homopolymers (polypropylene glycols) and EO/PO copolymers, as additives for WBM (as noted above), the use of PAGs including butylene oxide (BO) monomer for this purpose has not hitherto been proposed.

Alcohol alkoxylates such as alcohol ethoxylate (AET) (RO(EO)<sub>n</sub>H) have similarly been proposed as additives for WBM, while the use of such molecules including BO monomer has not been suggested for this purpose.

Suitable additives for use in the drilling fluid of the invention thus include EO/BO copolymers, PO/BO copolymers, and EO/PO/BO copolymers, possibly also including RO groups in the case of alcohol alkoxylates.

In order to retain an acceptable level of biodegradability, the molecules preferably generally contain at least 30 mol % EO, with the remainder comprising BO and optionally PO and/or hydrocarbon chains R.

The preferred additive molecules for use in the drilling fluid of the invention are copolymers of EO/BO, with the ratio of EO:BO being in the range 30:70 to 80:20 mol %.

In the case of alkoxylates, R is any suitable alkyl group, which may be a straight or branched chain. R is preferably in the range C<sub>4</sub> to C<sub>8</sub>. Longer hydrocarbon chains are preferably avoided for reasons of solubility and because they promote undesirable foaming of drilling muds.

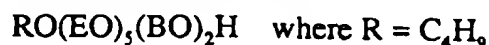
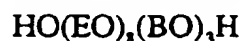
Random copolymers have better solubility than block copolymers and so are preferred.

Mixtures of polyols may be used.

The additive molecules generally have molecular weights of less than about 3000, and have substantial solubility in distilled water, seawater and potassium brines at ambient temperatures. In general, the molecules will exhibit cloud point behaviour at temperatures in the range 25 to 75°C, although this is not essential.

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Three typical additive molecules suitable for use in the drilling fluid of the invention are:



Additives for use in the invention are either commercially available, eg from Dowell Schlumberger, or can be readily synthesised.

The additives are typically used in WBM in amounts in the range 3 to 10% by weight, preferably 3 to 5% by weight.

The drilling fluid of the invention may otherwise be of conventional formulation, with the aqueous medium typically comprising fresh water, salt water, other salt solutions or mixtures thereof.

Other additives may be included in the drilling fluid in conventional manner. In particular, potassium ions, eg from potassium chloride, may be included to improve shale inhibition properties.

Drilling fluids in accordance with the invention have been found in laboratory tests to exhibit improved shale inhibition properties as compared with known polyol containing WBM, particularly in the absence of added potassium ions. This is environmentally advantageous, as discussed above.

The mechanisms of shale inhibition is not at present understood, but it is thought (without wishing to be bound by theory) that the improved shale inhibition properties obtained with the drilling fluids of the invention result from enhanced hydrophobic interaction between adjacent polyol molecules adsorbed on clay surfaces of shales due to the increased hydrophobicity of the polyol resulting from the presence of BO.

The invention will be further described, by way of illustration, in the following Example.

### Example

The level of shale inhibition provided by different drilling fluid additives and formulations is routinely assessed by a number of laboratory techniques. Tests such as cuttings dispersion and shale swelling are suitable for the rapid screening of new additives and are widely use in the industry. A good indication of the inhibitive properties of an additive can also be obtained by immersing clay films made from montmorillonite/water pastes in the test fluid and noting whether the film disperses, softens or remains intact. This approach is particularly suitable for screening low viscosity, water-soluble species such as polyols and the results correlate qualitatively with cuttings dispersion data.

The film immersion technique was used to compare the inhibitive properties of two typical polyol molecules of this invention with 3 established polyol inhibitors. All tests were carried out using solutions containing 5 wt % polyol. Two tests were carried out on each polyol: one using distilled water solutions and one using polyol dissolved in a 7% aqueous solution of potassium chloride. The films were immersed in the fluid for 16 hours before being recovered and their condition assessed visually.

The results of these tests are given in Table 1. The three conventional polyols used for comparison were polyethylene glycol (PEG), polyalkylene glycol (PAG) and an n-butanol ethoxylate (BET). The average molecular weights of these materials were approximately 600, 650 and 320, respectively. The PAG was a random copolymer of ethylene (EO) and propylene oxide (PO) with an EO:PO ratio of approximately 1:1. Two polyols used as examples of this invention were polydisperse mixtures with average compositions of  $\text{HO}(\text{EO})_8(\text{BO})_3\text{H}$  and  $\text{HO}(\text{EO})_7(\text{PO})_2(\text{BO})_2\text{H}$ . These polyols are referred to as EO/BO and EO/PO/BO, respectively, in Table 1.

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TABLE 1

TEST FLUID	CONDITION OF CLAY FILM AFTER EXPOSURE TO TEST FLUID
5% PEG	Swollen and dispersed
5% PEG/7% KCl	Firm and intact
5% BET	Swollen and dispersed
5% BET/7% KCl	Firm and intact
5% PAG	Soft but intact
5% PAG/7% KCl	Firm and intact
5% EO/BO	Firm and intact
5% EO/BO + 7% KCl	Firm and intact
5% EO/PO/BO	Firm and intact
5% EO/PO/BO + 7% KCl	Firm and intact

The results show that, in the distilled water environment, higher levels of inhibition can be obtained with the EO/BO and the EO/PO/BO polyols of the invention than with the conventional PEG, PAG and BET additives.



CLAIMS

1. A water-based drilling fluid comprising as additive one or more polyalkylene glycols or alcohol alkoxylates including butylene oxide monomer.
2. A drilling fluid according to claim 1, wherein the additive comprises one or more ethylene oxide/butylene oxide copolymers, propylene oxide/butylene oxide copolymers and ethylene oxide/propylene oxide/butylene oxide copolymers, possibly also including RO groups in the case of alcohol alkoxylates.
3. A drilling fluid according to claim 1 or 2, wherein the additive contains at least 30 mol % ethylene oxide, with the remainder comprising butylene oxide and optionally propylene oxide and/or hydrocarbon chains R.
4. A drilling fluid according to claim 2 or 3, wherein R is in the range  $C_4$  to  $C_{11}$ .
5. A drilling fluid according to claim 3 or 4, wherein the additive comprises copolymers of ethylene oxide/butylene oxide, with the ratio of ethylene oxide:butylene oxide being in the range 30:70 to 80:20 mol %.
6. A drilling fluid according to any one of the preceding claims, wherein the additive comprises random copolymers.
7. A drilling fluid according to any one of the preceding claims, wherein the additive comprises molecules having molecular weights of less than about 3000 and having substantial solubility in distilled water, seawater and potassium brines at ambient temperatures.
8. A drilling fluid according to any one of the preceding claims, wherein the additive comprises molecules exhibiting cloud point behaviour at temperatures in the range 25 to 75°C.

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9. A drilling fluid according to any one of the preceding claims, wherein the additive comprises one or more of the following:
- $\text{HO}(\text{EO})_8(\text{BO})_3\text{H}$   
 $\text{HO}(\text{EO})_7(\text{PO})_2(\text{BO})_2\text{H}$   
 $\text{RO}(\text{EO})_5(\text{BO})_2\text{H}$  where  $\text{R} = \text{C}_4\text{H}_9$
10. A drilling fluid according to any one of the preceding claims, wherein the additive is present in an amount in the range 3 to 10% by weight.
11. A drilling fluid according to claim 10, wherein the additive is present in an amount in the range 3 to 5% by weight.
12. A drilling fluid according to any one of the preceding claims, comprising aqueous medium of fresh water, salt water, other salt solutions or mixtures thereof.
13. A drilling fluid according to any one of the preceding claims, comprising one or more further additives.
14. A drilling fluid according to claim 13, comprising potassium salt additive.
15. A drilling fluid according to claim 14, wherein the potassium salt comprises potassium chloride.
16. A drilling fluid according to claim 1, substantially as herein described.

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C09K7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	GB,A,2 283 036 (BP CHEMICALS) 26 April 1995 see page 3, line 23 - page 4, line 35 see page 7, line 12 - line 31; claims 1-10; example 1 ---	1,2,4, 12-16
Y	US,A,3 396 105 (R.F.BURDYN) 6 August 1968 see column 3, line 51 - column 4, line 13 see column 10, line 56 - column 11, line 1 see claims 1,2; examples I,II ---	1,2,4, 12-16
Y	DE,A,43 02 462 (HENKEL) 30 June 1994 see page 3, line 46 - page 3, line 63 see page 5, line 23 - line 60 see page 7, line 3 - line 11; claims 1-5,15,16 ---	1,2,4, 12,13
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 495 579 (THE BRITISH PETROLEUM COMP.) 22 July 1992 see page 2, line 50 - page 3, line 17 see claims 1-8 -----	1,12-16

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